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Prompt and Delayed Electron Photoejection from Triamminecopper (I) and Formation of a Dinuclear Excited State Complex in Aqueous Solution

Kenneth L. Stevenson
Indiana University - Purdue University Fort Wayne

Pamela B. Bell
Indiana University - Purdue University Fort Wayne

PROMPT AND DELAYED ELECTRON PHOTOEJECTION FROM TRIAMMINECOPPER (I) AND FORMATION OF A DINUCLEAR EXCITED STATE COMPLEX IN AQUEOUS SOLUTION

Kenneth L. Stevenson, Pamela B. Bell, Ottó Horváth, Attila Horváth
(Kenneth L. Stevenson, Professor of Chemistry)
Department of Chemistry

Equilibrated $Cu(NH_3)_2^+$ and $Cu(NH_3)_3^+$ eject electrons when flashed with 266-nm laser light of 7 ns pulsewidth in aqueous ammonia solutions. Both prompt ejection (i.e. at times shorter than the laser pulsewidth) and delayed ejection (at times as long as several μs) are observed. An intermediate with a strong absorbance maximum at 400 nm is formed immediately after the pulse, and it decays with a lifetime that increases with concentration of the ground-state copper complex, suggesting and excited-state equilibrium reaction between the excited and the ground-state copper (I) complexes resulting in an excited dinuclear species such as an excimer or exciplex. It is proposed that the source of the delayed electron formation is the dissociation of the excited dinuclear species into a triplet monomeric excited state that decays by electron ejection.